

CATALYTIC DEALKYLATION OF TAR ACIDS

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Low-temperature carbonization has long been considered as a possible method for the utilization of lignite and other low-grade coals. Various fixed-bed processes were developed and tried prior to the first World War, but most of them met with limited success, and none became commercially significant. In the low-temperature carbonization process, the tar produced contains large quantities of tar acids. Depending on the coal carbonized and the conditions employed, the tar acids content of the tar will vary from around 15 to 50 percent. In the carbonization of Texas lignite, the distillable fraction of the low-temperature tar contains around 25 volume-percent tar acids of which only around 3 to 4 volume-percent are low-boiling phenols. The low-boiling tar acids, which are commercially obtained from coke-oven tar phenols, cresols, and xyenols have well-developed markets and uses and command a good price in the pure state. The market for the higher-boiling phenols or tar acids is limited, and when marketed as impure mixtures, they sell at a much lower price than the lower boiling phenols. Owing to the limited market for these high-boiling phenols, large quantities of these coke-oven tars containing tar acids are burned as residual fuel. Using fluidized-bed techniques developed during the last decade in the petroleum industry, workable low-temperature carbonization processes have been developed and offer great potentialities, providing that the market value of the carbonization products can be increased, for example, by converting high-boiling tar acids to low-boiling phenols.

Low-temperature tars have a high degree of alkylation. Methods of removing some or all of the alkyl groups, or decreasing their chain length, consequently are of considerable interest. One method of conversion presently under study by the Bureau of Mines is the catalytic dealkylation at atmospheric pressure in which the alkyl groups are split off from the phenolic ring, yielding lower boiling homologs. Numerous catalysts of the silica-alumina type developed for petroleum cracking are available for study. The ideal catalyst would naturally be one that promoted cleavage of the alkyl group--aromatic nucleus carbon-carbon bond at the same time avoiding rupture of the phenolic carbon-oxygen bond, which would result in a high yield of phenol itself. The Bureau plans to test individual catalysts at three temperature levels to determine the most promising catalyst and the best temperature range, which will then be more comprehensively evaluated to fix optimum operating conditions for maximum phenol yield.

Three types of catalysts were used in Bureau tests performed in the laboratory glass reactor in which low-boiling methanol solubles were dealkylated. A silica-alumina catalyst in pellet form gave yields of light phenols of approximately 30 volume-percent of the feed acids. The same catalyst, crushed to 16-20 mesh,

showed somewhat greater activity and yields. With cobalt-molybdenum catalyst, yields of light phenols were very low, and large amounts of gas and carbon were produced. With a cobalt catalyst, a fair yield of light phenols was obtained even though the total conversion was low.

Experimental

Catalytic Dealkylation Laboratory-Scale Apparatus. The Bureau's laboratory-scale glass dealkylation unit was set up as shown in the schematic diagram (Figure 1.). A picture of the apparatus is shown in Figure 2. A calibrated feed reservoir of 250-ml. capacity was connected to a small bellows-type pump whose stroke could be adjusted to deliver from 15 to 3,000 cc./hr. of liquid feed. The pump discharged through a length of 1/8-inch stainless-steel tubing entering the reactor through a glass feed tube inserted in the top head of the reactor. An earlier feed device was tried, consisting of a 100-cc. hypodermic syringe mounted over the reactor and in contact with a motor-driven rotating threaded rod, which slowly depressed the syringe plunger. During operation, the plunger repeatedly stuck in the syringe barrel resulting in intermittent feeding and breakage hazards. This method was used in Runs 4 and 5, and was then replaced by the pump.

The reactor unit was of all-glass construction, designed as shown in Figures 3 and 4. The body of the reactor was a cylinder approximately 1-1/4-inch O. D. by 1-inch I. D. and 36 inches overall length, fitted at top and bottom with standard taper glass joints. It was fabricated entirely from "Vycor" 96 percent silica glass, affording safe operation up to 900°C. Eight inches from the bottom of the tube, indentations were made in the tube wall to hold a perforated porcelain disk, which served as a catalyst support. The reactor head, made of Pyrex glass, had three taper joints at the top. Through the central taper joint, a Pyrex thermocouple tube was inserted, extending lengthwise through the reactor tube and terminating at the porcelain support. The feed inlet tube fitted into a second joint; the third was not used. There were two small side connections with spherical joints, one for the entering of the carrier gas and the other for a pressure tap connected to a mercury manometer for measuring the pressure drop across the reactor packing. The bottom adapter, also of Pyrex, served to connect the reactor to the product receiver, a 500-cc. Erlenmeyer flask of actinic glass, immersed in an ice bath. Exit gases passed off through a small side tubulure and were metered through a wet-test meter. A tube packed with glass wool was placed in the off-gas line to protect the meter against dust or carbon particles and entrained vapors.

The reactor was mounted vertically within an electrically heated furnace, 31 inches overall length with a heating zone 30 inches long, rated at 2,200 watts and operable to 1,850°F. Temperature adjustment and control were obtained with a variable transformer in the power supply to the furnace. This furnace was installed after Run 22. Before that, two smaller 750-watt furnaces, each 13 inches long, were mounted end-to-end to encompass the reaction zone. With this arrangement, an unheated zone occurred where the two units came together, causing heat losses at that point, consequently, a poor heat transfer. A more uniform heating was obtained using the larger furnace.

Helium was used as the carrier gas to maintain flow throughout the system and to sweep feed and product vapors through the reactor. The gas was supplied from cylinders through appropriate regulators; the flow rate was measured by a

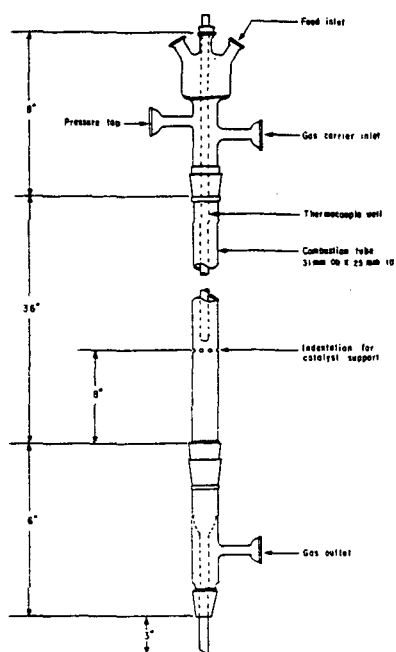


Figure 3. Dealkylation Glass Reactor.

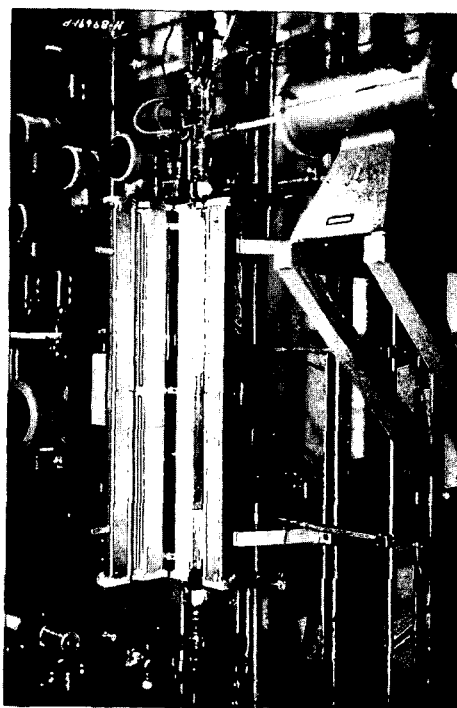


Figure 4. Picture of the Dealkylation Glass Reactor.

rotameter and was adjusted with a small needle valve at the rotameter inlet. Temperatures in the reactor were measured with chromel-alumel thermocouples connected to a Brown "Elektronik" six-point recording potentiometer. The pressure drop across the reactor packing, as noted before, was read on a mercury manometer connected across the inlet and outlet of the reactor.

In preparing for a test, the reactor tube and top head were assembled, and the thermocouple well was inserted. A weighed amount of catalyst was poured into the reactor through one of the openings in the top head. The height of catalyst above the support disk was measured, and the volume was calculated from calibration data previously obtained on the empty tube. Glass beads 4 mm. in diameter were poured on top of the catalyst to a convenient height, forming a preheating zone. The reactor was clamped into position within the furnace, and the necessary connections were made with the rest of the apparatus. Feed material was added to the feed reservoir. The specific gravity of the feed was determined at room temperature by weighing a graduated cylinder containing 100 ml. of feed.

Procedure. The tar acids for the dealkylation study were obtained from samples of low-temperature lignite tar supplied by the Texas Power and Light Company. The samples were products from a solvent extraction pilot plant in which hexane and methanol were used in a double-solvent operation to separate neutral and acidic components. Tar acids were recovered from the methanol extract by first stripping off solvent, then distilling the acids into two fractions designated as high-boiling and low-boiling methanol solubles.

We originally planned to use the total high-boiling methanol solubles for feed. This material was solid at room temperature and was therefore diluted with an equal volume of toluene to render it fluid and permit its pumping into the combustion tube of the glass reactor. With this feed, operating difficulties were caused by deposition of nonvolatile resinous substances, which plugged the reactor. Similar deposits occurred when a low-boiling methanol solubles residue boiling above 225°C. was used. Tar acids of intermediate boiling range did not cause any plugging. Because of its greater ease of handling, we decided to work with low-boiling methanol solubles. Samples of this stock were fractionated under vacuum on a Podbielniak high-temperature distillation apparatus using a 2:1 reflux ratio. The fraction boiling between 230°C. and 266°C. was retained as feed for the dealkylation study. In Runs 4 through 17, the feed was diluted with toluene; beginning with Run 18, the feed acids were used directly with no dilution (Table I).

The feed materials were analyzed for total acids by extraction with 10 percent caustic solution, considering the total caustic-soluble portion as phenols. The first batch of feed distillate showed 97.5 volume-percent tar acids, whereas the second batch analyzed only 82.0 volume-percent. A third feed fraction, not yet used, showed 81.0 volume-percent acids. The variation in the first material was probably owing to insufficient mixing before sampling, and for subsequent tests, the feeds should be fairly uniform.

Catalysts were commercial types furnished by various manufacturers. In most of the tests, a silica-alumina cracking catalyst, Socony-Vacuum TCC type 34 "Durabead," was used. Its composition is about 90 percent silica and 10 percent alumina, with less than 0.1 percent contaminants, which are primarily sodium salts. The catalyst comes in bead form and was sized to -4, +6 mesh before using.

Table 1. Laboratory-Scale Catalytic Dehydration of Tertiary Acids.

Run number	4	5	6	7	9	10	11	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Catalyst type	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	b	b	c	c	c	d
Catalyst weight, g.	87.0	92.6	116.8	116.8	94.8	94.8	84.4	83.4	83.4	83.4	80.5	80.5	80.5	80.5	80.5	83.8	81.6	152.7	152.7	152.7	174.8
Catalyst volume, cc.	131	143	165	165	137	137	134	134	134	134	121	121	121	121	121	127	128	128	128	132	132
Condition of catalyst	New	New	New	Regen.	New	Regen.	New	Regen.	New	Regen.	New	Regen.	New	Regen.	New	Regen.	Mixed	New	Regen.	New	Regen.
Length of run, hrs.	1.08	1.55	3.00	2.67	1.08	1.58	2.08	2.12	2.00	2.10	1.17	1.55	0.92	1.80	1.63	1.60	1.70	1.50	1.45	1.50	1.35
Feed composition	e	f	g	g	g	g	g	g	g	g	h	i	i	i	i	i	i	i	i	i	j
Total feed, ml.	--	99	199	120	223	216	222	204	228	212	199	171	168	168	164	158	168	148	141	136	149
Total feed, g.	89	93	186	112	205	204	209	193	215	201	184	160	167	166	163	157	167	147	140	135	149
LHSV, vol. total feed/ vol. catalyst/hr.	--	0.44	0.40	0.28	1.51	1.00	1.03	0.73	0.80	0.79	0.71	1.21	0.90	1.51	0.77	0.79	0.78	0.77	0.76	0.71	0.84
Carrier gas flow rate, SCFH	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36
Operating conditions	1-9	0	0	0-5	0-65	0-50	0-98	0-48	0-68	0-18	0-74	0	0	0	0	3	3	2	0	0	0
Reactor ΔP, mm. Hg	--	800	539	683	489	543	607	844	891	839	843	456	640	518	748	724	781	507	569	615	727
Preheat temperature, °F.	839	--	825	824	842	783	835	712	702	759	711	688	699	675	703	746	703	788	704	860	762
Top catalyst temperature, °F.	840	800	826	823	813	800	847	821	821	825	825	829	825	828	825	828	825	832	754	832	906
Bottom catalyst temperature, °F.	--	86	181	101	201	204	205	189	214	194	180	160	154	164	158	149	138	157	124	122	109
Liquid product, ml.	72	79	165	93	186	186	190	174	197	182	166	148	153	161	155	148	136	122	120	104	138
Liquid product, g.	--	6.84	11.53	9.81	7.03	8.32	5.63	7.90	8.81	7.22	8.75	4.49	6.58	5.69	6.66	7.05	9.04	5.73	19.30	15.40	21.0
Carbon deposited, g.	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

a Soceny-Vacuum "Durabead," silica-alumina, 4-6 mesh.
b Soceny-Vacuum "Durabead," silica-alumina, 16-20 mesh.
c Girder G-35B, cobalt molybdenum on alumina, 3/16" tablets.
d Girder T-300, cobalt molybdenum on alumina, 1/8" tablets.
e 50 vol. % toluene + 50 vol. % 230-266°C. LIMS-1 (97.5% acetic acid).
f 50 vol. % toluene + 50 vol. % 230-266°C. LIMS-1 (97.5% acetic acid).
g 50 vol. % toluene + 50 vol. % 230-266°C. LIMS-1 (97.5% acetic acid).
h 50 vol. % toluene + 50 vol. % 230-266°C. LIMS-1 (97.5% acetic acid).
i 100 vol. % 230-266°C. LIMS-1 (97.5% acetic acid).
j 100 vol. % 230-266°C. LIMS-2 (62.0% acetic acid).

In Runs 21, 22, and 23, the catalyst was ground and a -16, +20 mesh portion was used. The two other catalysts used up to now were Girdler G-35B, in 3/16-inch tablets, containing 13-1/2 weight-percent cobalt and molybdenum on an alumina support; and Girdler T-300, in the form of 1/8-inch tablets containing about 60 percent cobalt on kieselguhr. All three catalysts were used as received.

Helium carrier gas was admitted to the system from the supply tank, adjusting the flow rate to 0.36 SCFH. Power was applied to the furnace and the temperature, as measured by the bottom catalyst bed thermocouple, was gradually raised to the desired operating temperature. When the temperature was stabilized at the desired level, the feed pump was turned on to start the run. The liquid feed stream coming into contact with the preheat zone vaporized and passed downward over the packed catalyst. The cracked vapors entered the product receiver, cooled by an ice bath, where the liquid product collected and helium and noncondensable product gases passed off to the gas meter.

The run was continued until sufficient liquid product was collected for analysis. Depending on the charge rate, a run lasted from one-half to 3 hours. Pertinent operating data were recorded on log sheets at 10 to 15 minute intervals. After feed was discontinued at the end of a run, helium flow was maintained, and the reactor was kept at temperature for about an hour to purge the reactor completely of all vaporizable products.

The total liquid product was weighed, its volume was measured at room temperature, and it was then distilled using a glass Vigreux column 1/2-inch in diameter and 10 inches long. An initial fraction, boiling up to 160°C. (Table II) was distilled at atmospheric pressure. A second fraction with a boiling range of 160°-230°C. was distilled at 10 mm. Hg pressure. The tar acids content of this fraction was determined by extraction with sodium hydroxide solution. The amount of tar acids thus determined was considered the total yield of light phenols. Tar acids in the distillation residue were similarly determined. The acids in the caustic extract were recovered by neutralizing the extract with dilute sulfuric acid and were retained for possible future analysis.

During the cracking operation, considerable carbon was deposited on the catalyst. This carbon was removed by burning it off in an air stream, thus regenerating the catalyst. The reactor was brought to 1,000°F. on helium; air was then substituted for helium at a rate sufficient to maintain 1,050° to 1,100°F. during the regeneration. Carbon dioxide produced was absorbed in an absorption bulb packed with "Ascarite." The absorption bulb was preceded by a small tube, was packed with cupric oxide, and was heated to 700°C. by a small mortar, which converted any carbon monoxide to the dioxide. Drying tubes containing "Drierite" placed before and after the cupric oxide tube trapped any water vapor in the gas stream. The total weight of carbon dioxide formed was then taken as a measure of the carbon formed in the run, assuming that the catalyst deposit consisted entirely of carbon.

Discussion and Conclusions

The study on dealkylation of tar acids undertaken at the Bureau's Morgantown Research Center was concerned chiefly with the selection of a most effective catalyst for the production of low-boiling phenols and the examination of different variables in determining the maximum yield. This is a preliminary study. Not all of the

Table II. Fractional Distillation of the Dealkylated Tar Acids

Run number	4	5	6	7	9	10	11	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Yields, wt. % of feed																						
Liquid product	80.7	85.1	88.8	82.5	90.7	91.6	90.8	90.2	91.5	90.4	89.8	92.7	91.8	96.1	93.5	91.0	86.7	93.8	83.3	85.5	78.5	93.1
Carbon	--	7.4	6.2	8.7	3.4	4.1	2.7	4.1	1.1	3.6	4.7	2.8	3.9	3.4	4.0	4.3	5.7	3.4	13.2	11.0	15.5	9.7
Gas + loss (by difference)	--	7.5	5.0	8.8	5.9	4.3	6.5	5.7	1.4	6.0	5.5	4.5	4.3	0.5	2.5	4.7	7.6	2.8	3.5	3.5	6.0	-2.8
Distillation of liquid product																						
IBP - 160°C., vol. %	--	68.7	60.9	64.3	56.8	53.2	58.6	59.0	53.3	59.2	57.2	56.7	7.5	5.5	7.6	9.8	14.4	7.1	9.7	7.4	13.5	6.3
160 - 230°C., vol. %	--	8.6	6.6	6.8	2.7	2.2	3.4	10.6	17.3	17.5	16.0	20.5	41.5	35.0	36.8	29.5	35.8	12.6	5.2	12.4	2.6	25.4
Residue > 230°C., vol. %	--	18.3	30.0	24.0	40.3	--	36.0	30.7	21.0	23.3	25.4	22.2	49.6	56.9	54.2	59.8	48.6	79.4	84.2	77.9	81.9	67.2
Tar acids in 160 - 230°C. fraction, vol. %	--	73.2	78.3	65.2	58.3	66.7	51.1	87.0	90.0	89.5	88.5	80.6	79.2	80.0	84.0	85.6	88.0	82.3	73.3	80.0	--	82.2
Tar acids in residue, vol. %	--	83.0	--	--	--	--	--	--	--	--	--	--	--	66.6	68.0	70.0	63.0	75.5	78.0	78.0	78.0	80.0
Total conversion, vol. % feed acids	--	73.6	--	--	--	--	--	--	--	--	--	--	--	68.9	61.4	63.5	60.9	72.6	42.5	43.6	46.1	47.6
Yield light phenols, vol. % feed acids	--	10.9	9.6	7.6	2.9	2.8	3.3	17.4	29.8	29.3	26.2	31.4	31.0	27.9	29.7	23.6	28.2	9.9	3.3	8.8	<2.6	23.7

variables (such as temperature, space velocity, catalyst size, catalyst regeneration characteristics, type of feed stock, use of additives to feed such as steam or pyridine, etc.) were examined, and more research work will follow to study and determine the results of these variables.

The following conclusions can be drawn from the actual studies on the dealkylation of tar acids:

1. Tar acid feed stocks containing high-boiling residua are not suitable for dealkylation studies because they form nonvolatile, resinous deposits that plug the reactor. Fractions of intermediate boiling range did not form plugs, and successful tests were carried out using tar acids boiling from 230° to 266°C.
2. Silica-alumina catalyst, typified by Socony-Vacuum TCC-34 "Durabead," is very effective in dealkylation of high-boiling phenols to lower boiling homologs. Yields of around 30 volume-percent of feed acids were obtained operating at around 825°F. and with liquid hourly space velocities of about 0.8.
3. Girdler G-35B, a cobalt-molybdenum catalyst, appears unsatisfactory for dealkylation of tar acids because of low phenol yields and considerable losses of feed to carbon and gas.
4. A high-cobalt catalyst, Girdler T-300, showed possibilities of being highly selective in light phenol production, providing total conversion of feed acids can be increased.
5. The new laboratory-scale glass dealkylation unit (Fig. 1) has been shown to be suitable for carrying out catalyst screening tests and for future evaluation studies on individual catalysts.

Reference to specific commercial brands, materials, or models of equipment in this article is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.